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EVALUATION OF CHLORINATED HYDROCARBON CATALYTIC REDUCTION TECHNOLOGY

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16. ABSTRACT The report gives results of a laboratory evaluation of a control technique developed for the EPA for the catalytic reduction of chlorinated hydrocarbons (specifically PCBs and chlorinated pesticides such as heptachlor and endrin). The technique involves elution of polluted water at ambient temperature and at neutral pH through a column containing a mixture of sand and copper iron catalyst. The evaluation found that PCBs are not detectably reduced, but are chromatographically eluted from the column in order of increasing chlorination. The catalyst was found to partially reduce heptachlor and endrin. The possibility of chromatographic elution by endrin and/or heptachlor was briefly investigated using miniature columns and found to be insignificant. The report also describes the observation of an additional on-site demonstration of the catalytic reduction technology, including observation of the test procedure, gas chromatography with electron capture detection, and subsequent laboratory GC/MS analysis of transported samples. An evaluation of the reports generated during the development of the catalytic reduction technique is presented. It discusses errors and omissions in the developmental experimental protocol which led to the erroneous conclusions that the technique was applicable to PCBs.

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ABSTRACT

A control technique developed for the Environmental Protection Agency for the catalytic reduction of chlorinated hydrocarbons (specifically polychlorinated biphenyls [PCBs] and chlorinated pesticides such as heptachlor and endrin) was evaluated under laboratory conditions. The technique involves elution of polluted water at ambient temperature and at neutral pH through a column containing a mixture of sand and copper/iron catalyst. The evaluation found that PCBs are not detectably reduced, but are chromatographically eluted from the column in order of increasing chlorination. Thus, early column eluate fractions were found to contain only the lower chlorinated PCBs, giving the illusion that partial reduction had occurred.

The catalyst was found to partially reduce heptachlor and endrin. The carbon skeleton remained intact and chlorines were successively replaced by hydrogens. In a stirred flask of the catalytic mixture and pesticide-spiked water at 60°, the reaction was found to be only partially successful with most of the products accounted for as the parent compounds or the analogs representing loss of one chlorine.

The possibility of chromatographic elution of endrin and/or heptachlor was briefly investigated using miniature columns and found to be insignificant. A degradation product of heptachlor upon standing in water was found to be not heptachlor epoxide, but rather $C_{10}H_9Cl_5O_2$ (tentative)--apparently a dihydroxy derivative of heptachlor.

An additional on-site demonstration of the catalytic reduction technology was observed by an RTI and an EPA representative. This program included observation of the test procedure, gas chromatography with electron capture detection and subsequent GC/MS analysis of transported samples at the RTI laboratory.

An evaluation of the reports generated during the development of the catalytic reduction technique is presented. It discusses errors and omissions in the developmental experimental protocol that led to the erroneous conclusions that the technique was applicable to PCBs.

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ABBREVIATIONS

A-1016	--	Aroclor®-1016
ESC	--	Envirogenics Systems Company, El Monte, California
GC/ECD	--	Gas Chromatography/Electron Capture Detection
GC/MS	--	Gas Chromatography/Mass Spectrometry
PCB	--	Polychlorinated Biphenyl
TCB	--	2,3',4',5-tetrachlorobiphenyl
CIS	--	Copper/Iron/Sand

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SECTION I
INTRODUCTION

In an effort to assist industry in compliance with legislation concerning the permissible levels of toxic substances in industrial water effluents, the EPA has undertaken to develop various control technologies which may be applied by industry. An example of this research is the catalytic reduction of chlorinated hydrocarbons (specifically PCBs and chlorinated pesticides such as heptachlor and endrin). Under a contract to Envirogenics Systems Company (ESC), El Monte, CA (EPA Contract No. 68-03-2364), a technique for the chemical removal of PCBs from water was investigated whereby the aqueous PCB solution is passed through a column containing sand and a copper/iron catalyst at ambient temperature and pressure.

Experiments by Envirogenics indicated successful removal of PCBs from water; however, a test at the Gulfbreeze, FL, EPA laboratories discovered the column effluent was toxic to fish. Analysis of effluents of the process by Gulfbreeze-EPA and Bionomics detected little or no changes in the concentration of PCBs as compared to the feed solutions.

The purpose of this project was to chemically evaluate the technique. Aqueous solutions of PCBs and chlorinated pesticides were analyzed before and after treatment with the copper/iron catalyst and examined for changes in their composition. The main analytical technique used in this study was electron capture gas chromatography (GC/EC), which showed whether or not changes had occurred in the chlorinated compounds. When a species change was noted, the more sophisticated technique of gas chromatography-mass spectroscopy (GC/MS) was used to identify the species. Samples were analyzed for iron and copper in solution, and as a check for evidence of catalytic dechlorination, samples were analyzed for ionic chloride.

SECTION II

SUMMARY AND CONCLUSIONS

The catalytic reduction technology was evaluated (according to the procedures provided by the developing laboratory) for PCBs and found totally ineffective. In essence, the column (160 cm x 37 mm i.d.) behaves as a large chromatographic column, requiring on the order of 40 bed volumes (30ℓ) to elute all components of the Aroclor® -1016 feed solution. No evidence of catalytic reduction of PCBs was observed.

The reduction technique was also briefly evaluated for endrin and heptachlor. To facilitate the evaluation, the reductions were carried out in stirred round bottom flasks at elevated temperature (~60°) for extended times (4-6 hours). Partial reduction was observed at these elevated temperatures. GC/MS analysis of highly concentrated batches indicated that the endrin and heptachlor were being reduced by successive replacement of chlorine by hydrogen. No evidence for changes in the carbon skeleton were observed. The extent of dechlorination, even under these highly favorably conditions, was slight. Although all of the $C_{12}H_xCl_yO$ analogs were found, including the tentative identification of some $C_{12}H_{14}O$ and related hydrocarbons, $C_{12}H_8Cl_6O$ (endrin) and various isomers of $C_{12}H_9Cl_5O$ accounted for greater than 80% of the total ion current response in the GC/MS. The evaluation of the reduction of heptachlor and endrin thus showed that the technique worked, although apparently not well enough to efficiently reduce the pesticide to hydrocarbons and mono- and dichlorinated species which may be biodegradable.

The progress reports generated by the development laboratory were evaluated to determine the errors and omissions in the experimental protocol which led the investigators to erroneous conclusions about their results. A list of the points of criticism is presented.

SECTION III
RECOMMENDATIONS

Based on the findings of the research presented herein, it is recommended that no further effort be made to develop and/or implement on a pilot scale the technology for catalytically reducing PCBs. The brief evaluation of the reduction of heptachlor and endrin by this technique also indicated that the technique is insufficient for generating low- or non-chlorinated organics which are bio-degradable. Thus, it must be conclusively shown that reduction is complete before any attempts at commercial application are undertaken.

Any further research and development of the chemical reduction of chlorinated hydrocarbons in water utilizing copper/iron catalyst must first address the chemistry of the reactions. Basic research should be carried out to understand the mechanism(s) and kinetics involved before any work at optimizing the conditions can be undertaken. Once the chemistry is well defined, the types of compounds for which the catalyst would be effective, and thus reaction conditions, may be predicted.

SECTION IV

MATERIALS AND METHODS

COLUMN PREPARATION

The columns for the PCB work were constructed of Fisher and Porter Lab-Crest 37 mm i.d. Pyrex tubing with a stopcock at the bottom and 0.5 cm bed of glass wool. The column packing was prepared by blending the copper catalyzed iron powder and sand supplied by Envirogenics Systems Company in a ratio of 1:3.6. The packing was poured into the column to a depth of 160 cm and the intersticies filled with water. The void volume (or bed volume) of the column was determined to be 750 m . This column will hereafter be referred to as the copper/iron/sand (CIS) column. A duplicate column was prepared in a similar way using sand without the copper/iron powder.

EXTRACTION

Previous experience in these laboratories (1) has shown that PCBs are much more soluble in toluene than in hexane and thus are more readily extracted from a variety of media, including water, using toluene. Accordingly, aliquots of the column effluent and influent were extracted using toluene as follows: a 100 mℓ aqueous aliquot was extracted three times with 20 mℓ portions of toluene in a separatory funnel. The combined toluene extracts were dried over sodium sulfate and concentrated on a hot plate in a flat bottom boiling flask with a Snyder column, followed by blow-down under a nitrogen stream at 25°. This recovery procedure has been demonstrated in our laboratory to be quantitative.

ANALYSIS

All gas chromatography-electron capture detection (GC/ECD) analyses were performed on a Fisher Victoreen 4400 gas chromatograph with a ^{63}Ni electron capture detector. GC/MS analyses were obtained using a Finnigan

3300 quadrupole GC/MS with a PDP/12 computer. The determination of Cu and Fe was carried out on a Perkin Elmer 603 Atomic Absorption Spectrophotometer equipped with deuterium background correction. Chloride ion determinations were accomplished using a chloride ion-specific electrode on an Orion 801A Digital Ionalyzer.

SECTION V

EVALUATION OF PCB REDUCTION TECHNOLOGY

Solutions of PCB mixtures (Aroclor®-1016 and 2,3',4',5-tetrachlorobiphenyl [TCB]) were passed through two columns in parallel experiments. One column held the CIS mixture, while the second held only sand. A condensed sampling schedule is shown in Table 1.

TABLE 1

Fraction #	Feedstock	Volume (ℓ)	Cumulative Volume	Description
0	A-1016	0.75	0.75	Void volume
2	A-1016	0.1	1.35	
5	A-1016	0.1	2.9	
20	A-1016	0.1	14.3	
31	TCB	0.3	16.8	Change of feedstock
37	TCB	0.4	17.9	
39	TCB	2.0	21.9	
40	Distilled water	2.0	23.9	Attempt to flush column
41	Distilled water	0.1	24.0	

After 14.6ℓ (20 bed volumes) of Aroclor solution had been passed through the column, subsequent chromatograms of the eluate fractions were essentially identical to one another. At that point, the feedstock was changed to TCB because it is a single polychlorinated species and thus easier to trace than the complex Aroclor mixture.

After 5.4ℓ (7 bed volumes) of TCB solution had been passed through the column and no TCB could be found in the eluate, the column was flushed with 2ℓ (2.7 bed volumes) of distilled water. Next, a 0.1 portion of distilled water was passed through and analyzed.

The results of this experiment, summarized in Figure 1, indicate clearly that chromatographic elution is taking place on the CIS column. The lower chlorinated isomers (which have shorter GC retention times) eluted more quickly than the higher isomers. The lower chlorinated isomers are more water soluble than the higher chlorinated molecules, and this would account for their passing through the column more quickly. After passing 28ℓ (37 bed volumes) through the column, all isomers present in the A-1016 were observed, although the last major peak (RT ≈10.2 min) had just begun to elute and was present only as a shoulder on the adjacent peak (RT ≈9.4 min). The isomers which eluted between 4-8 minutes were present in higher concentration since they were not as easily stripped from the column during feed of water and TCB solutions. The identification of the major peaks in Fraction 41 (the distilled water fraction) was confirmed by GC/MS using multiple ion detection. The TCB, which was first applied to the column about 15ℓ before the experiment was terminated, was never observed in the column eluate. This is to be expected in light of the chromatographic behavior of the higher isomers (also tetrachlorobiphenyls) in Arochlor® - 1016.

In the parallel experiment, Aroclor® - 1016 and TCB solutions were eluted through a column containing sand only. The results of this experiment were similar to those observed for the CIS column, although the elution appeared to be slightly faster. Typical gas chromatograms illustrating the chromatographic elution of successive components of A-1016 are shown in Figure 2.

To determine the significance of long contact time within the column, two successive fractions were collected from the CIS column 65 hours apart. No significant reduction had taken place after this lengthy interruption of flow.

The above experiments clearly illustrate that both the CIS column and the sand column act as crude liquid chromatographic columns. Because of their greater aqueous solubility, the lower chlorinated isomers in the PCB mixture pass through first. The disproportionate amount of lower chlorinated species in the initial eluates from the CIS column could lead to the erroneous conclusion that the higher chlorinated species are being dechlorinated.

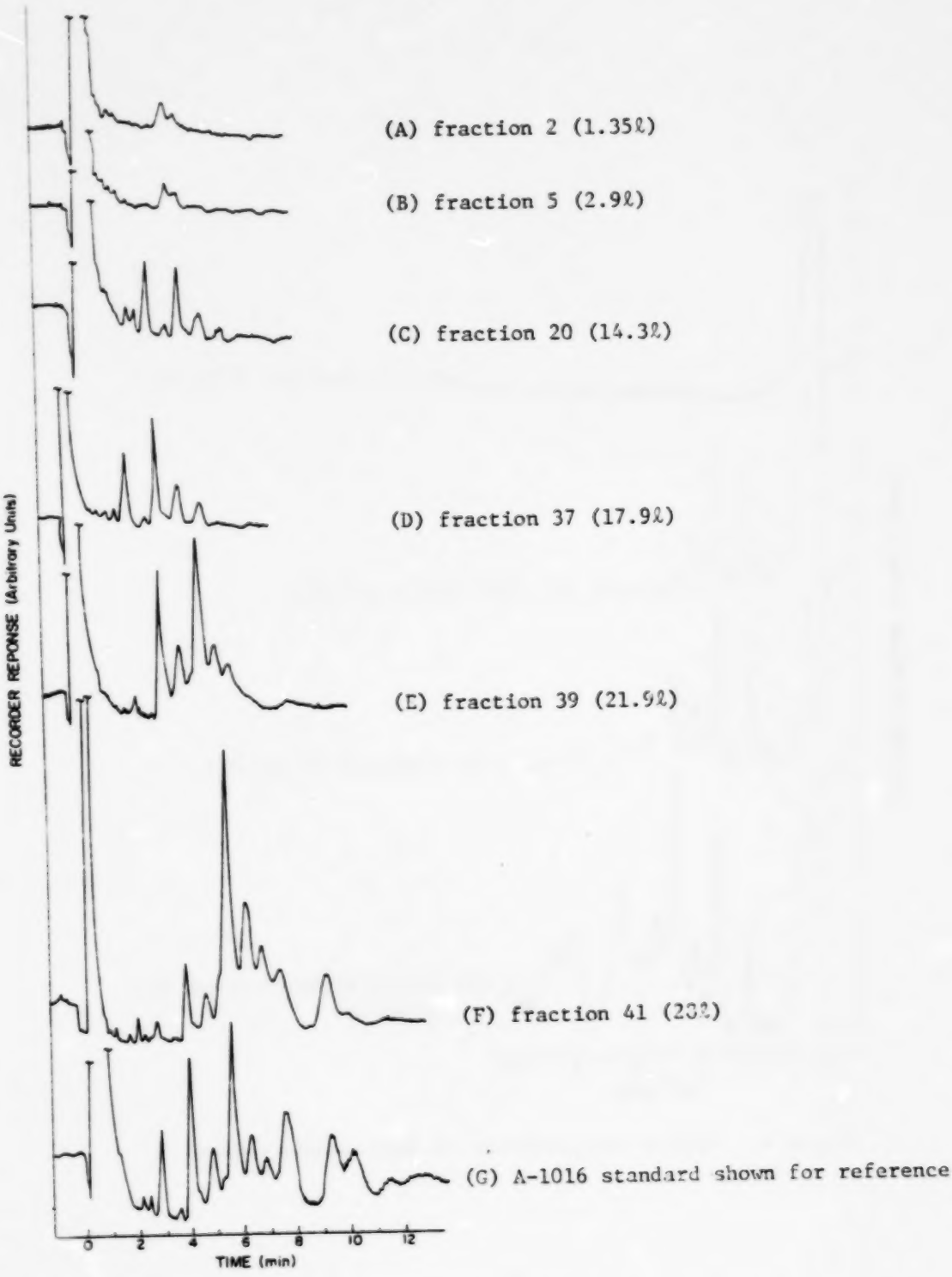

Figure 1. GC/ECD chromatograms of CIS column eluates.

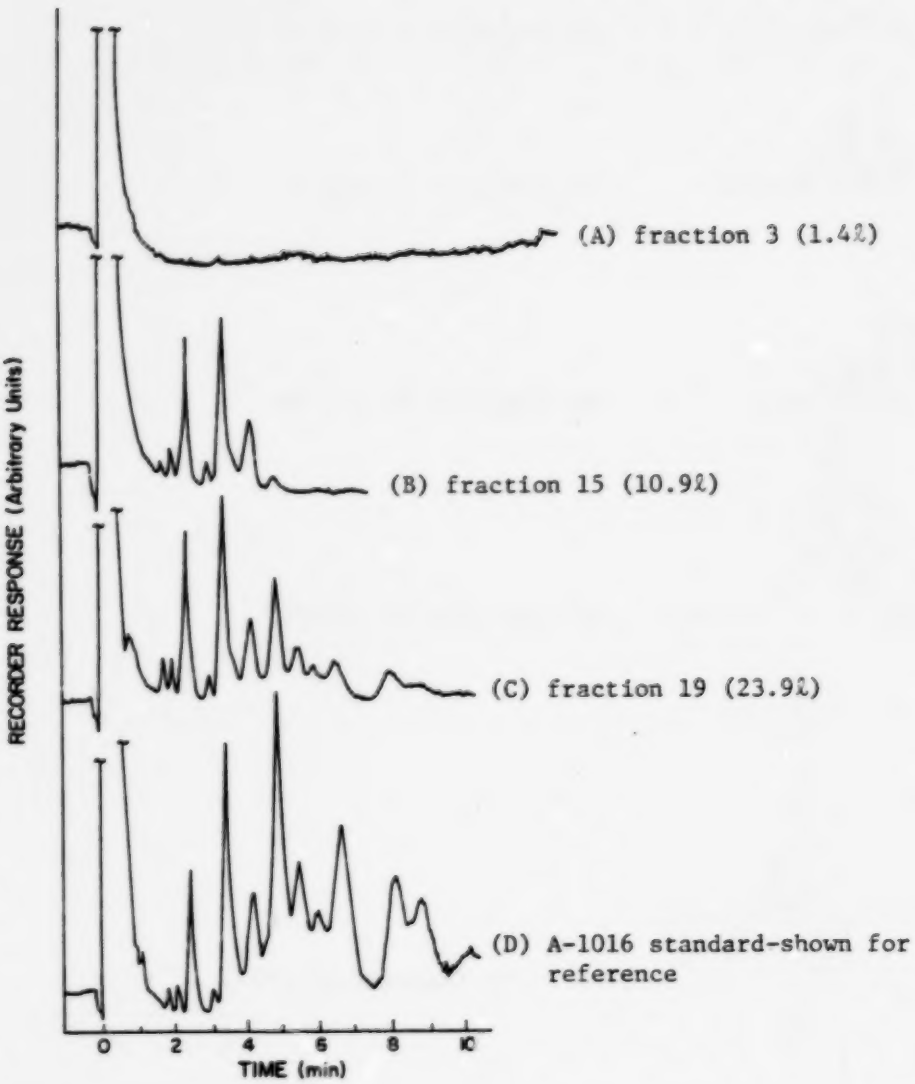

Figure 2. GC/ECD chromatograms of sand column eluates.

Only the 2,3',4',5-tetrachlorobiphenyl (TCB) fed onto the column remained unaccounted for. It was suspected that this material and A-1016 were adsorbed on the column packing. At the conclusion of the elution experiments, 50 g of column packing was collected from the top of each column, vacuum filtered to remove the aqueous portion, and extracted with toluene. The results of this experiment show clearly in both cases, large amounts of TCB in the gas chromatogram, although large volumes of non-TCB-containing water had passed through the column (8.1ℓ or 11 bed volumes in the case of the CIS columns and 17.1ℓ in the case of the sand column) and several days had elapsed. This presents further evidence that reductive degradation is not occurring to any appreciable extent.

The concentrations of chloride, as measured using a chloride ion-selective electrode, were below the detection limit (~5 ppm) in all samples analyzed. Since this measurement yielded no useful information, it was discontinued. In all fractions analyzed by atomic absorption, the iron concentrations were found to be less than 0.3 ppm and the copper concentrations less than 0.01 ppm. The consistently low concentrations of iron and copper in the effluent do not support a reductive mechanism in which iron is an indicator of reduction.

SECTION VI

EVALUATION OF ENDRIN/HEPTACHLOR REDUCTION

STIRRED FLASK EXPERIMENTS

The catalytic reduction performance of the copper/iron/sand mixture was also evaluated for endrin and heptachlor. At the request of the project officer, the reduction effects were first evaluated by the stirred flask technique.

An experiment was performed with three parallel solutions of endrin and heptachlor in: (a) a flask containing the copper/iron/sand mixture (50g); (b) a flask containing sand; and (c) a flask which contained the endrin/heptachlor solution only. All three flasks were heated to 60° and stirred for not less than 4 hours. GC/ECD analysis of the reaction mixtures after several hours indicated that some degradation of endrin and heptachlor may have taken place (Figure 3). Since the loss of heptachlor and concurrent appearance of another peak at RT ≈ 7 min* was observed in both the flask containing sand and the flask containing solution only, this reaction cannot be attributed to catalytic reduction by the copper/iron/sand mixture.

This peak was, in fact, observed in extracts of the stock solution after storage at 5° for two days. Analysis of this extract by GC/MS indicated heptachlor (RT ≈ 7 min*) and endrin (RT ≈ 11 min*). The mass spectrum of the unknown peak at RT = 8 min* led to a tentative structural assignment of $C_{10}H_9Cl_5O_2$. The lack of a parent ion precludes a definitive assignment. This compound would be a product of addition of two water molecules and loss of two chlorines, an unusual reaction, especially under these mild conditions.

The presence of this compound has been reported numerous times in the literature (3-5) as a degradation product of heptachlor in water. The compound has been identified in these reports as 1-hydroxychlordene ($C_{10}Cl_6H_6O$, m/e = 352). Further analytical characterization, beyond the scope of his project, is needed to resolve the apparent discrepancies and assign a structure to this compound.

*Retention times were different in the GC/ECD and GC/MS analyses because of differences in the column temperatures.

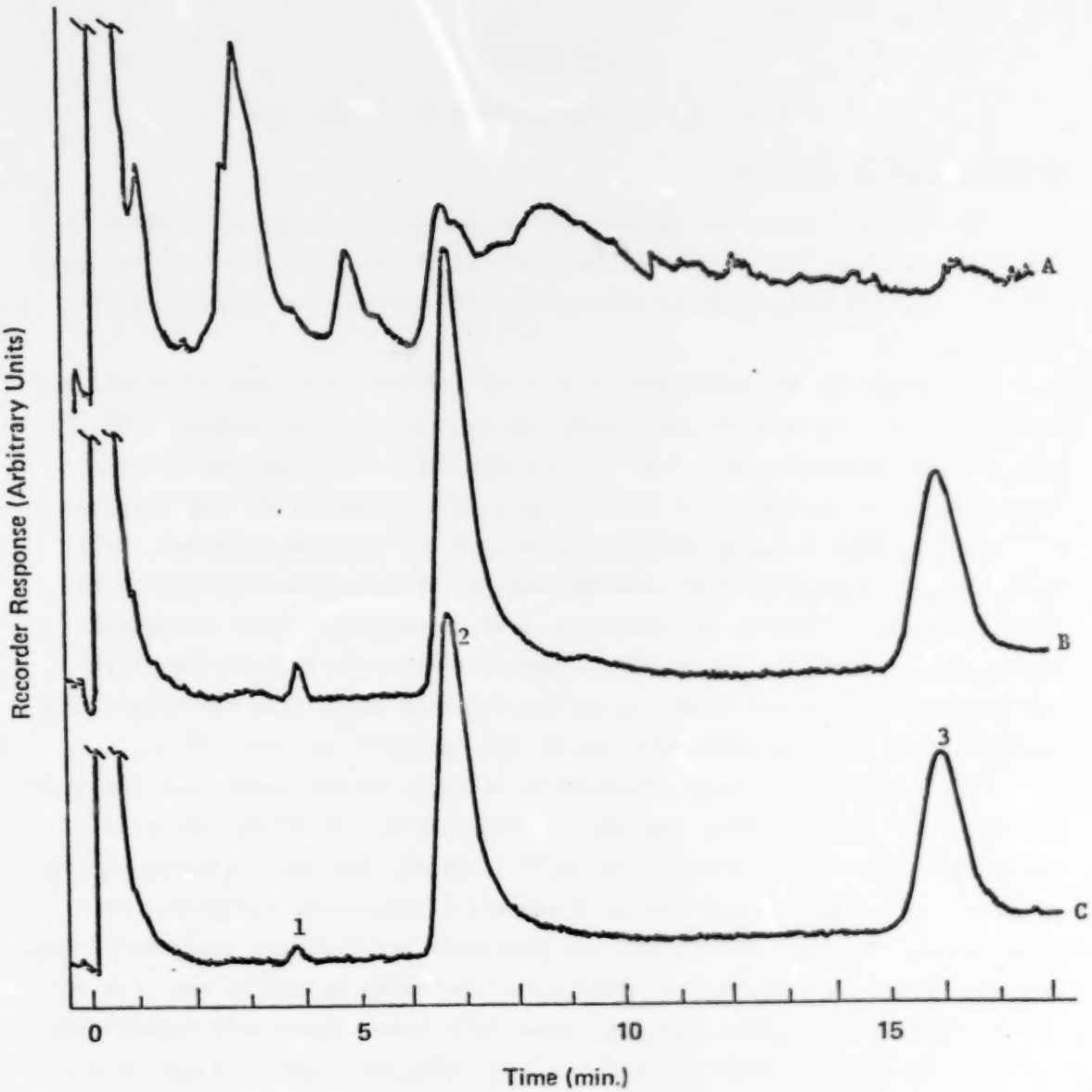

Figure 3. Chromatograms (GC/ECD) of endrin/heptachlor reduction. Experiment No. 1 in a stirred flask.
Top: A--copper/iron/sand + endrin and heptachlor aqueous solution
Center: B--sand + endrin and heptachlor aqueous solution
Bottom: C--endrin and heptachlor aqueous solution only
1: heptachlor
2: $C_{10}H_9Cl_5O_2$ (tentative--see text)
3: endrin

In a second experiment the effects of temperature were investigated and it was found (Figure 4) that the degradation was substantially more marked at 60° than at 25°. Thus, degradation of heptachlor and endrin was established as being related to the presence of the copper/iron mixture, although the degradation products were unknown. A third flask, containing distilled water and the copper/iron/sand mixture, was used as a blank in this experiment. The GC/ECD analysis of an extract showed no contamination of the blank, as expected.

To establish the identity of the degradation products, a reaction was carried out with much larger amounts of endrin and heptachlor to yield enough of the reaction products for GC/MS analysis. The solubility limit of endrin and heptachlor was exceeded during this experiment. The results of this experiment (Table 2) demonstrated that several dechlorinated heptachlor and endrin species as well as some oxygenated analogs were present. There was no evidence of complete (or even nearly complete) dechlorination or of a reverse Diels-Alder type reaction to form chloro-cyclopentadienes.

Experiment 3 indicated the complexity of the reaction products, so a further experiment with endrin alone was conducted to elucidate the reduction products of this single starting material. A large batch (19 mg) of endrin was reacted at 60° in a stirred flask and analyzed by chemical ionization mass spectrometry. The results, shown in Figure 5, and Table 3, indicate that endrin is catalytically degraded (i.e., replacement of chlorine by hydrogen) to some extent, although the vast majority of the reaction product is found as $C_{12}H_8Cl_6O$ (endrin) and $C_{12}H_9Cl_5O$.

Dechlorinated endrin ($C_{12}H_{14}O$) was tentatively identified although the amount found is minor compared to the higher chlorinated analogs. Thus, even under much more severe reaction conditions than recommended, the catalytic reduction is far from complete.

The results of the stirred flask experiments show that endrin and heptachlor were catalytically reduced by the successive replacements of chlorine by hydrogen in the presence of the copper/iron/sand catalyst. However, the evidence indicated that, even at 60° for 4 hours, this process was far from

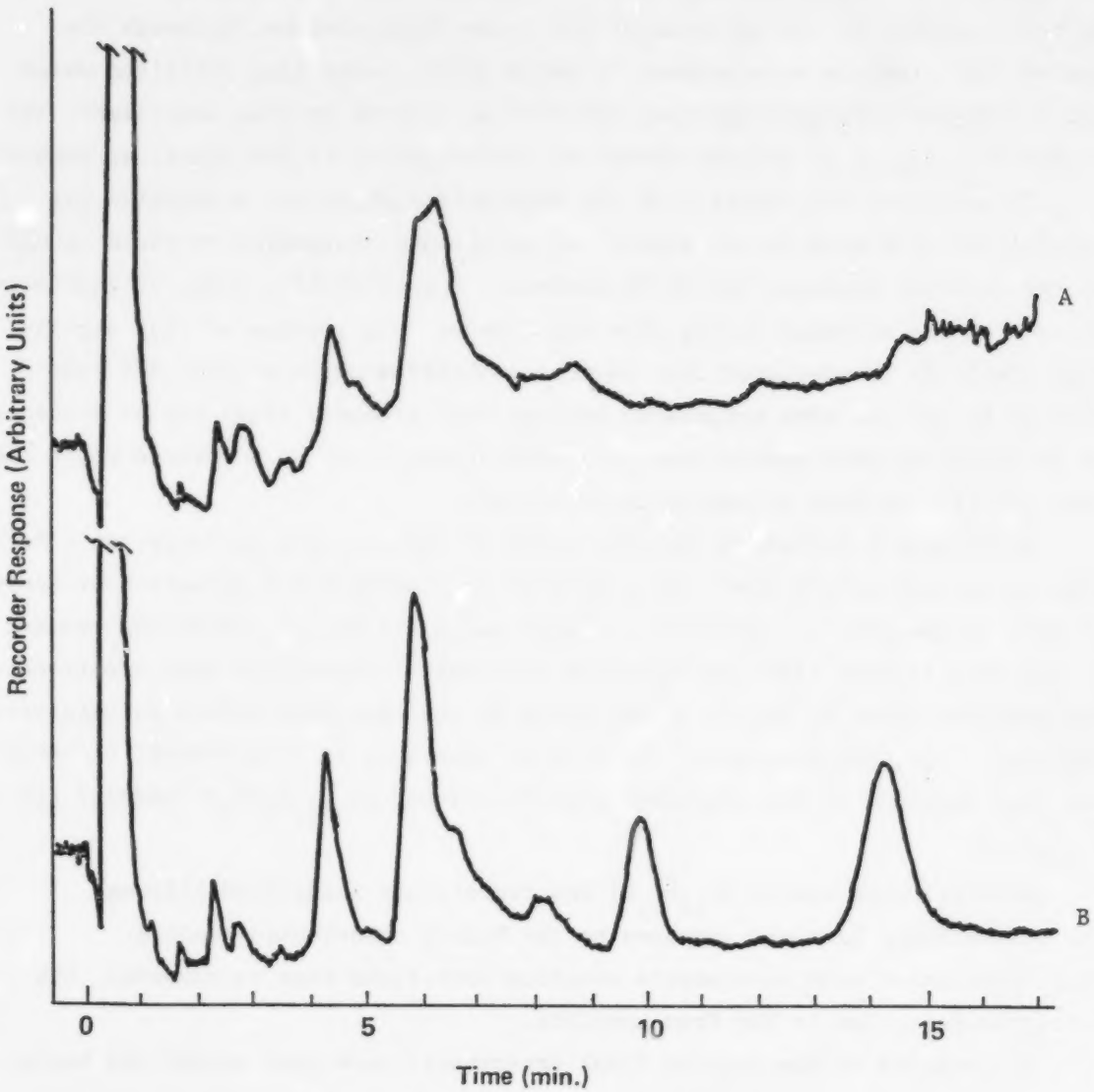

Figure 4. Chromatograms (GC/ECD) of endrin heptachlor reduction. Experiment No. 2 in a stirred flask:
A. Mixture reacted at 60° in presence of copper/iron/sand
B. Mixture reacted at 25° in presence of copper/iron/sand.
See figure 3 for peak assignments.

TABLE 2

COMPOUNDS IDENTIFIED IN ELECTRON IMPACT GC/MS ANALYSIS OF ENDRIN/HEPTACHLOR REDUCTION (Experiment 3)

Compound	Retention Time (min)	Integrated Response (%)[b]
$C_{10}H_7Cl_5$	4.0 - 4.4	0.2
$C_{10}H_6Cl_6$	4.9 - 5.6	1.2
$C_{10}H_7Cl_5O$ (tent)[a] and $C_{10}H_5Cl_7$ (heptachlor)	6.4 - 7.3	4.6
$C_{10}H_6Cl_6O$	7.3 - 7.7	1.8
$C_{10}H_9Cl_5O_2$ (tent)[c]	7.7 - 8.6	25.9
$C_{12}H_{10}Cl_4O$	8.8 - 9.4	0.3
$C_{12}H_9Cl_5O$	9.4 - 9.8	1.9
$C_{12}H_8Cl_6O$ (endrin)	9.8 -10.8	17.2
$C_{12}H_8Cl_6O$[c]	10.8 -13	47.0

[a] Mass spectral quality was too poor for definitive assignments.

[b] Response values are listed as a percent of the summed integrated areas for each peak in the chromatogram. These values may correspond approximately to relative concentration although no molar response factors are available.

[c] Differences in fragmentation and chromatographic retention times indicate at least two isomers with this molecular formula are present in addition to endrin.

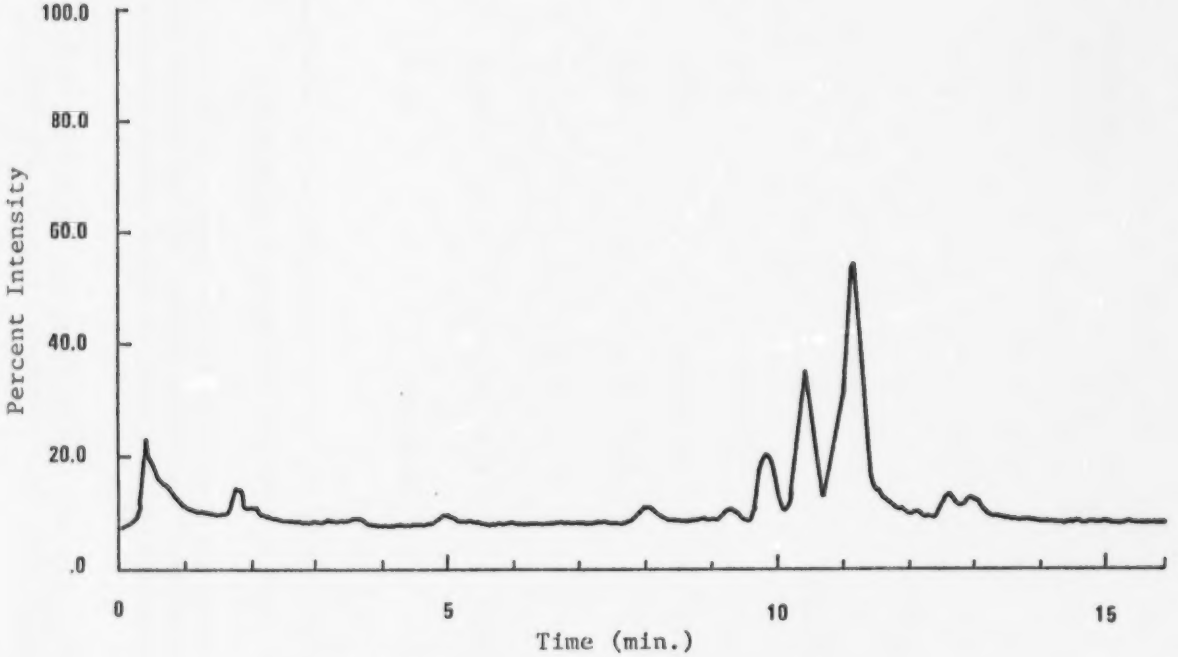

Figure 5. Total ion current chromatogram of chemical ionization GC/MS analysis of products from catalytic reduction of endrin (Experiment 4). See Table 3 for identification.

TABLE 3

COMPOUNDS IDENTIFIED IN CHEMICAL IONIZATION GC/MS ANALYSIS OF ENDRIN REDUCTION (Experiment 4)

Compound	Retention time[a] (min)	Integrated Response (%)[b]
$C_{12}H_{12}O$, $C_{12}H_{14}O$ and $C_{12}H_{16}O$ (tent.)	1.3 - 2.8	4.4
$C_{12}H_{13}ClO$	3.0 - 3.9	1.1
$C_{12}H_{12}Cl_2O$	4.4 - 5.9	2.0
$C_{12}H_{11}Cl_3O$	6.2 - 7.0	0.8
$C_{12}H_{10}Cl_4O$	7.7 - 9.5	6.1
$C_{12}H_9Cl_5O$	9.6 - 10.7	32.7
$C_{12}H_8Cl_6O$ (endrin)	10.8 - 11.7	45.6
$C_{12}H_9Cl_5O$	12.4 - 13.3	7.4

[a]Retention times represent boundaries of the integration. Some compounds represent two or more isomers, as evidenced by multiple peaks in the chromatogram.

[b]Response values are listed as a percent of the summed integrated areas for each peak in the chromatogram. These values may correspond approximately to relative concentration although no molar response factors are available.

complete. These results indicate that a column reduction at room temperature with a much shorter contact time would have produced even less dechlorination of endrin and heptachlor. This hypothesis was tested as described below.

MINIATURE COLUMN EXPERIMENTS

The reduction of heptachlor and endrin by the copper/iron/sand mixture was tested using 18 cm x 1.0 cm i.d. (14.1 ml) columns. Two columns were prepared in parallel: one of the copper/iron/sand mixture and one of the sand only. The void volume of the columns was determined to be 7 mℓ . A mixture of heptachlor and endrin (200 µg/ℓ of each) was prepared in pH=7 water and eluted through the columns.

The sand column was found to be inert. The column effluent contained endrin, heptachlor, and the compound tentatively identified as $C_{12}H_9Cl_5O_2$ (vide supra).

The copper/iron/sand column exhibited some reduction as shown in Figure 6. The extent of reduction, however, is minor in comparison with the stirred flask reactions. Even upon sitting in the column for about 65 hours, endrin and heptachlor are clearly visible and the predominant peak in the chromatogram corresponds to the compound previously tentatively identified as $C_{10}H_9Cl_5O_2$. Thus, even with extremely long contact time, the reduction is incomplete and merely represents partial substitution of the chlorines.

SUMMARY EVALUATION OF ENDRIN AND HEPTACHLOR REDUCTION

Both the stirred flask and miniature column experiments demonstrated some catalytic reduction of heptachlor and endrin. The extent of reduction, however, is slight even when experimental conditions are much more severe (higher temperature and/or longer times) than those used in the developing lab.

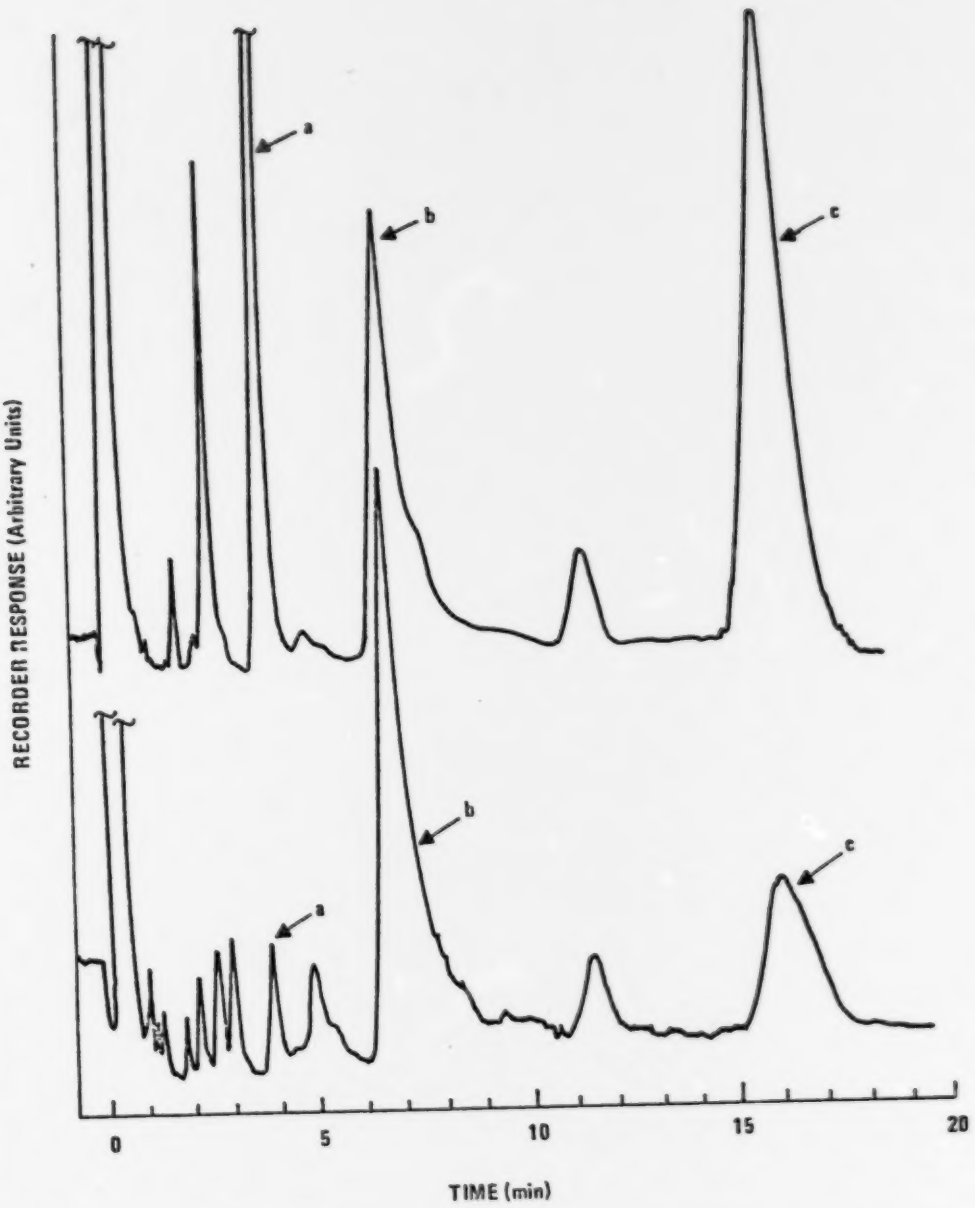

Figure 6. Gas chromatograms of endrin/heptachlor reduction experiments using miniature copper/iron/sand column.
A. Column effluent after 3300 mℓ--typical of all fractions
B. Column effluent after 3500 mℓ--after standing in column for 65 hrs.
Compound identification: a) heptachlor, b) $C_{12}H_9Cl_5O_2$, c) endrin.

SECTION VII

CRITIQUE OF MONTHLY REPORTS OF CONTRACT NO. 68-03-2364

The reports generated during the development of the catalytic reduction technology have been evaluated. A list of errors and omissions which led to the erroneous conclusion that the technique was applicable to PCBs follows:

1) No preliminary feasibility studies (kinetics, thermodynamics, mechanisms, etc.) were carried out to determine whether the catalytic reduction could take place at ambient temperature and pressure.

2) It is disturbing that this technology was found to be unsuccessful in batch (stirred flask) reactions (see January 1976 report). One would expect the same type of reaction in a flask unless the process is a function of chromatography on the column. No attempt was made by the development laboratory to explain this observation.

3) The suggested increased efficiency of the column as a function of the mesh size (and therefore surface area) of the sand supports the theory that adsorption is the process rather than reduction. However, there was no extraction of the solid bed material to investigate this possibility.

4) Observations of the chromatograms of the inlet (feed) and outlet sample from the March, Gulf Breeze (Bionomics) study yielded the conclusion that both chromatograms were essentially identical. No significant reduction was achieved. This was proved subsequently by toxicity data and the high concentration of PCBs in Bionomics' Control samples.

5) There was no identification of reaction products (although a GC/MS study was mentioned in the reports), and no attempt was made to do a complete mass balance across the column. Mass balances for chloride were conducted in several cases by turbidity. Chloride ion balances at these concentration levels (at or near the limit of detectability) by a turbidometric procedure are difficult at best.

6) A carefully designed experiment should have included blanks, controls (for example, a column packed with sand only) and internal standards. These were lacking in the work done by the development laboratory.

7) Based on the size of the columns and the possibility of a chromatographic mechanism, the number of void volumes (water) passed through the column were insufficient. Extended runs should have been made in order to mimic plant conditions.

Evaluation and justification of catalytic technology in the developmental portion of the program was primarily based on gas chromatography/electron capture detection. Interpretation of gas chromatograms on inlet and outlet samples (Gulfbreeze, Florida) demonstrated the difficulties and problems associated with the lack of GC/MS confirmation. A stricter control of the development phase with supporting documentation of the degree of dechlorination by GC/MS would have controlled boundary conditions of the experimental program.

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1. M.D. Erickson, R. A. Zweidinger, L. C. Michael and E. D. Pellizzari, "Environmental Monitoring Near Industrial Sites: Polychloronaphthalenes," EPA-560/6-77-019, July 1977.

2. Personal Communication, K. H. Sweeney, Envirogenics Systems Company, El Monte, California, April, 1977.

3. A. S. Y. Chan, J. D. Rosen, and W. P. Cochrane, Bull. Environ. Contamin. Toxicol., 6, 225-230 (1971).

4. A. Demayo, Bull. Environ. Contamin. Toxicol., 8, 234-237 (1972).

5. J. J. Eichelberger and J. J. Lichtenberg, Environ. Sci. Technol., 5, 541 (1971).

APPENDIX

On-site Demonstration by Envirogenics of a Catalytic Reduction Process for Endrin/Heptachlor.

INTRODUCTION

This appendix describes the on-site test procedures, and the analytical results of a catalytic reduction process of endrin/heptachlor. An RTI and EPA representative observed the demonstration by Envirogenics of the technology, on-site sampling and analysis by GC/EC, and returned concentrated aliquots of the feed materials, blanks and eluates to RTI laboratories for GC/MS analysis.

The "Test Procedure" section of this appendix was copied verbatum from an Envirogenics Systems Company experimental procedures manual.

TEST PROCEDURE

ENDRIN AND HEPTACHLOR REDUCTION
ENVIROGENICS DEMONSTRATION TESTS

COLUMN REDUCTION

Two aqueous solutions will be used, one containing approximately 100 ppb of endrin, and the second approximately 30 ppb of heptachlor. Each solution will be passed through separate copper-catalyzed iron columns at approximately 35 mℓ/min using freshly-prepared columns (37 mm by 1600 mm bed), each containing 600 g of copper-catalyzed iron powder and 2150 g of sand. Samples of the catalyzed iron and sand will be provided EPA or RTI if desired. The runs will be for a sufficient period to provide material for GC/MS analysis. Both the endrin and heptachlor solutions will also be passed through sand columns and eluate samples will be collected and analyzed.

ANALYSIS

Envirogenics intends to analyze the samples for endrin and heptachlor by electron capture and flame ionization detection gas chromatography, for chloride by turbidity, and iron and copper by atomic absorption spectrometry. For purposes of the chloride analysis, it will be necessary to wash all columns with water before use. It may be advisable to establish a chloride blank from the eluates of the endrin and heptachlor solutions passed through the sand columns. In order to avoid losses of organic material from the dilute aqueous phases by sorption on the container walls, the samples will be extracted with hexane immediately. The extractions will be made with Burdick and Jackson glass-distilled hexane of a single lot. The extracts will be analyzed by EC-GC, composited (unless the result is an obvious sport, in which case an additional sample would be drawn), and concentrated for GC/MS and FID/GC in Kuderna-Danish evaporators. The extracted aqueous samples would be retained for concentration and chloride analysis.

Small samples of the extracted effluent will be taken also for iron and copper analyses. These samples would acidified and analyzed for iron and copper by atomic absorption spectroscopy.

DETAILED PROCEDURE

Columns

The 37 mm dia x 1800 mm long glass tubes will be thoroughly cleaned and the glass wool mat put in place. For the reduction tests, 2150 g of type 30 sand and 600 g Fe/Cu will be blended and placed in the glass tube. The bed will then be washed with 1 ℓ acetone, drained, and filled with water by bottom feed. Deionized water (2 ℓ) will then be passed through the column. The sand column to be operated in parallel with the reductant column will be prepared by placing 2150 g sand in the same sized, similarly prepared column. The beds will be examined and suitably treated to remove air bubbles before starting flow.

Column Feeding

The endrin feed would be sampled at the beginning of the test, after 6-8 ℓ flow, and after 12 ℓ flow. Each sample would be 500 mℓ, and would be extracted with 3-50 mℓ portions of hexane. In making the extractions, it is important that no aqueous phase be carried over into the organic phase, so that if phase separation is difficult, 5 mℓ of 2% aqueous Na_2SO_4 may be added to promote separation of the layers. One mℓ portions of the extract will be reserved for EC/GC analysis, and the remainder composited and concentrated to 1.5 mℓ in the Kuderna-Danish evaporator. The 1.5 mℓ concentrate will be divided with EPA/RTI taking 1.0 mℓ and Envirogenics 0.5 mℓ. In addition, 1.3 ℓ portions would be sampled for chloride (and the 3-1/3 ℓ samples combined), and 25 mℓ samples would be taken for AA. The heptachlor feed would be sampled similarly.

COLUMN RUNS

General

The columns will be started and adjusted to a flow of 30-40 mℓ/min. Both the reductive column and sand column are to be running simultaneously. The flow valves will be adjusted to give a static head of ~15 cm. It is important that the column be kept covered with water at all times.

The first 2-1/2 ℓ of flow will be required to replace the water in the column at the start, and will not be extracted. However, a sample will be taken for chloride analysis.

Endrin and Heptachlor

A total of 15 ℓ of endrin solution will be run through the reduction column and the sand column. Each 3 ℓ of effluent will be collected, extracted with three 200 mℓ portions of hexane, and 1 mℓ of the extract taken for EC/GC. If the result is not a sport, the extracts will be combined and concentrated in the Kuderna-Danish to 1.5 mℓ (from the total 3 ℓ of hexane extracts). If any sample is obviously out of line (gross contamination, etc.), then an additional 100 mℓ will be drawn, extracted with three 10 mℓ portions of hexane, and reanalyzed as a check. The sample would then either be composited or rejected by mutual agreement. If rejected, the test would be continued for an additional 3 ℓ. The 3 ℓ sample after extraction will have a 1 ℓ sample retained for chloride analysis. In addition, a 25 mℓ sample will be taken for AA. The AA samples will be acidified with 1 mℓ conc HCl.

At the conclusion of the test (15 ℓ), a 2-1/2 ℓ portion of deionized water (post wash) is passed through the column, and the column allowed to drain. A 1 ℓ portion of glass-distilled acetone is then passed through the column, drained, and analyzed by EC/GC. The 1 ℓ acetone washes are continued until the effluent analysis is clear.

The heptachlor test will be carried out similarly, except that a total of 50 ℓ will be passed through the reduction column and the sand column.

ON-SITE GAS CHROMATOGRAPHY

All feed solutions for endrin and heptachlor were analyzed three times during the experimental phase to document the integrity of the stock (Figures C-1A and C-1B). The on-site demonstration of the technology for endrin and heptachlor used one common feed solution to feed both the sand and Fe/Cu columns. In addition, the concentration of the feed solution was determined by comparison to standard endrin solution to within 4% of the theoretical feed solution. Aliquots were analyzed from the effluent Fe/Cu and sand columns periodically during the tests to follow the extent of reaction. Six samples were concentrated following GC/EC analysis for later GC/MS analysis. These included endrin feed, endrin Fe/Cu effluent, endrin sand effluent, heptachlor feed, heptachlor Fe/Cu effluent, and heptachlor sand effluent. All gas chromatographic analyses were performed on a Perkin Elmer gas chromatograph with an electron capture detector. Data reduction was via a Hewlett Packard data system. Two gas chromatographic columns (OV-17 and DC-200) were utilized for analysis. The results of the on-site gas chromatography analyses are as follows:

1) Both endrin and heptachlor feeds compare with stock standards in purity. The gas chromatographic retention times of the stock endrin (6.50 minutes) and heptachlor (2.15 minutes) are the same for the feed solutions (Figures C-1A and C-1B).

2) No conversion or reaction was observed in either sand column (without Fe/Cu catalyst) for endrin (Figure C-2A) or heptachlor (Figure C-3A), i.e., the major peak observed was parent endrin (Figure C-1A) or heptachlor (Figure C-1B).

3) Immediate changes in the eluate GC/EC chromatograms for both endrin (Figure C-2B) and heptachlor (Figure C-3B) were observed for the Fe/Cu catalyst containing columns.

4) Effluent from the Fe/Cu endrin column experiment was shown not to contain parent endrin. This was demonstrated by injections of endrin (sand column effluent, Figure C-4A) and effluent from the Fe/Cu column (Figure C-4B) on an additional gas chromatographic column (DC 200). An equal volume injection of the sand and Fe/Cu effluent (Figure C-5) on DC-200 is included to show the difference in retention time. Presence of parent is not eliminated based on the retention times of the margin peaks on the OV-17 gas chromatographic column (Figures C-2A and C-2B). The absence of parent compounds was confirmed later by GC/MS analysis.

5) Following the addition of endrin and heptachlor feed to two separate Fe/Cu columns, the columns were washed with water and stripped with acetone. GC/EC chromatograms of the acetone wash indicated the presence of additional electron capturing species.

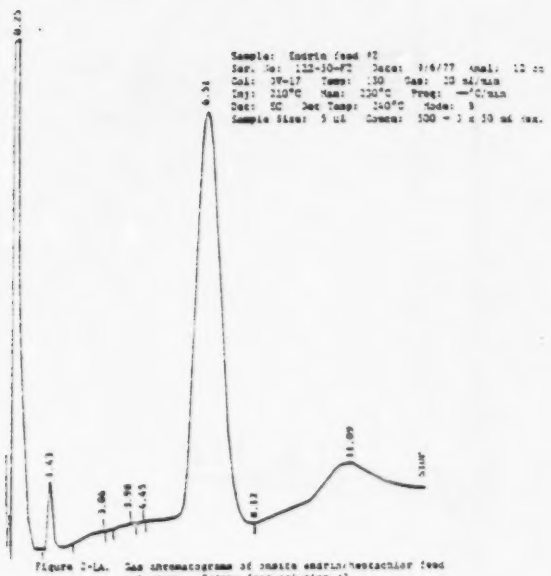
Sample: Enertia feed #2
Ser. No: 122-30-#2 Date: 9/6/77 Anal: 10 cc
Col: SW-17 Temp: 130 Gas: 30 ml/min
Inj: 210°C Max: 230°C Prog: —°C/min
Det: EC Det Temp: 240°C Mode: 3
Sample Size: 5 µl Concn: 300 = 3 x 10 ml tex.

Figure 3-1A. Gas chromatograms of zeolite enertia/tetrachlor feed solutions. Enertia feed solution #2.

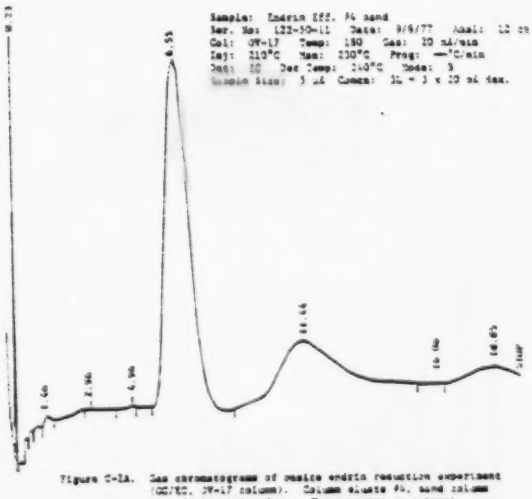
Sample: Enertia Eff. #4 sand
Ser. No: 122-30-11 Date: 9/6/77 Anal: 10 cc
Col: SW-17 Temp: 130 Gas: 30 ml/min
Inj: 210°C Max: 230°C Prog: —°C/min
Det: EC Det Temp: 240°C Mode: 3
Sample Size: 5 µl Concn: 3L = 3 x 10 ml tex.

Figure 3-2A. Gas chromatograms of zeolite enertia reduction experiment (OC/EC, SW-17 column). Column eluate #4, sand column (see figure 1A). Note: Chromatogram is typical of all fractions.

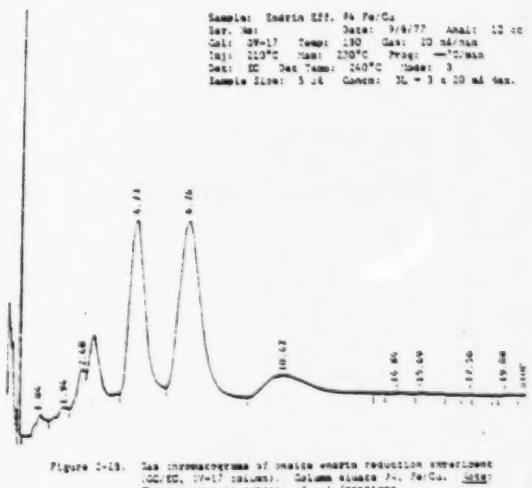
Sample: Enertia Eff. #4 Fe/Ca
Ser. No: Date: 9/6/77 Anal: 10 cc
Col: SW-17 Temp: 130 Gas: 30 ml/min
Inj: 210°C Max: 230°C Prog: —°C/min
Det: EC Det Temp: 240°C Mode: 3
Sample Size: 5 µl Concn: 3L = 3 x 10 ml tex.

Figure 3-2B. Gas chromatograms of zeolite enertia reduction experiment (OC/EC, SW-17 column). Column eluate #4, Fe/Ca. Note: Chromatogram is typical of all fractions.

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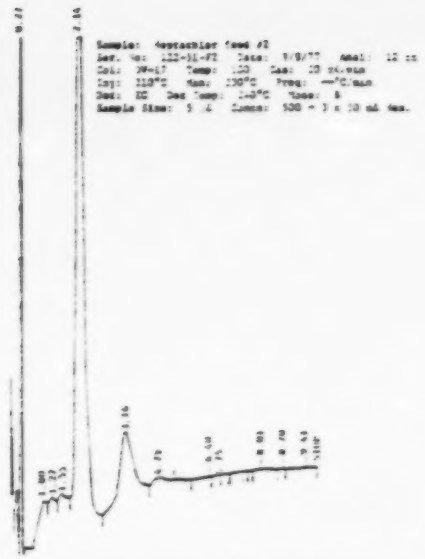

Figure I-18. Gas chromatograms of crude endrin reduction reaction solutions. Heptachlor feed solution #2.

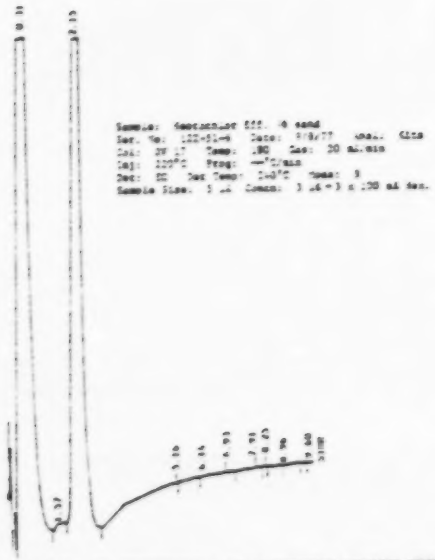

Figure I-19A. Gas chromatograms of crude heptachlor reduction experiment (DC, DC, SW-17 column). Column clumps P6, some column and Figure I-19: Note: Chromatograms is typical of six fractions.

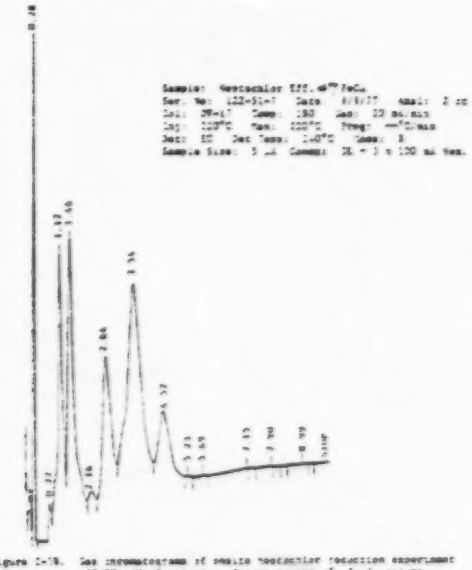

Figure I-19. Gas chromatograms of crude heptachlor reduction experiment (DC DC, SW-17 column). Column clumps 7, Fe Cu column. Note: Chromatograms is typical of six fractions.

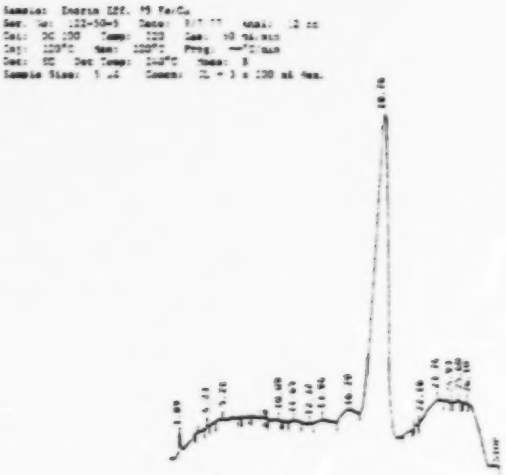

Figure I-4A. Gas chromatograms of enzyme reduction experiment, sand and Fe/Cu column (SC:EC, 3C=1:3). Enzyme effluent #5. Sand column. Note: Effluent from sand column identical to enzyme feed solution.

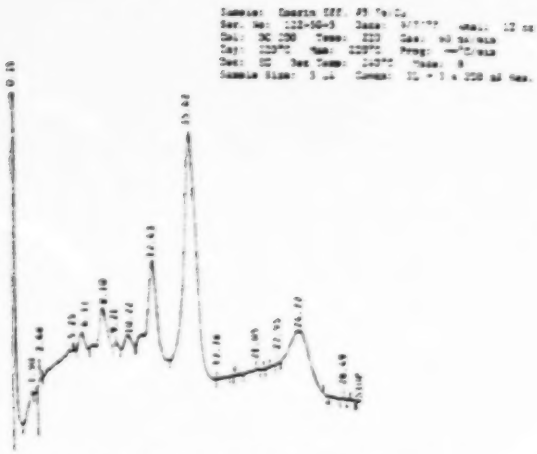

Figure I-4B. Gas chromatograms of enzyme reduction experiment, sand and Fe/Cu column (SC:EC, 3C=1:3). Enzyme effluent #5. Fe/Cu column.

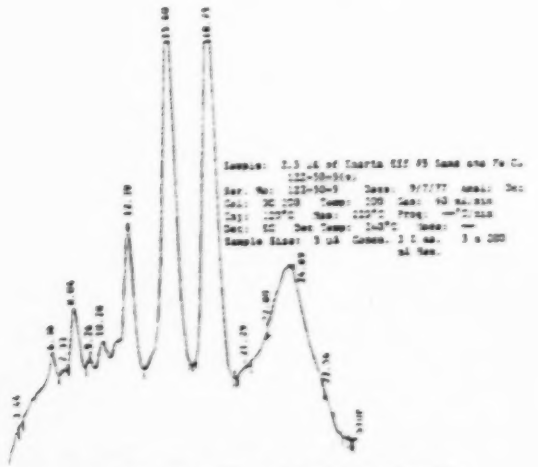

Figure I-5. Gas chromatograms of enzyme reduction experiment Fe/Cu column (SC:EC, 3C=1:3). Enzyme effluent #5 Fe/CU column + equal volume (spiked) of enzyme sand column effluent. Note: See Figure 4 for enzyme #5 Fe/CU effluent and enzyme sand column effluent on 3C 200.

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GC/MS ANALYSIS

INSTRUMENTATION AND ANALYSIS TECHNIQUE

GC/MS analyses were obtained using a 180 cm x 0.2 cm i.d. glass column packed with 2% OV-101 on Chromosorb W-HP maintained at 120°C for 3 minutes, then programmed at 12°C/min to 230° and held there for the duration of the run. The flow rate was 20 mℓ/min helium. GC/MS chromatograms were obtained using a Finnigan 3300 quadrupole GC/MS with a PDP/12 computer.

SUMMARY OF RESULTS

The results of the GC/MS investigation of six samples obtained during the on-site demonstration are as follows:

1) Heptachlor feed - The only species and only major substance found was heptachlor (see Figure C-6).
2) Heptachlor sand column - The only chlorinated species found was heptachlor (see Figure C-7). However, the sample was heavily contaminated with C_{22} and greater hydrocarbons.
3) Heptachlor Fe/Cu eluants - The chlorinated species observed are listed below.

Figure C-9. Heptachlor eluate concentrated to 1.0 ml.

Retention Time (min)	Tentative I.D.	Characteristic Ions
7.91	$C_{10}H_7Cl_5$	236,238,240,302,304,306
8.33	$C_{10}H_7Cl_5$	236,238,240,302,304,306
9.66	$C_{10}H_xCl_{4+n}$	283,285,287
9.91	$C_{10}H_xCl_{4+n}$	236,238,240

Figure C-8. Heptachlor eluate concentrated to 100 µl.

Retention Time (min)	Tentative I.D.	Characteristic Ions
4.73	$C_{10}H_9Cl_3$	168,170,172,234,236
6.41	$C_{10}H_xCl_{3+n}$	168,170,172
6.66	$C_{10}H_7Cl_5$	236,238,240,201,203,205, 301 to 310
7.00	$C_{10}H_7Cl_5$	236,238,240,201,203,205, 201 to 310
7.41	?	218,220,222
8.16	?	283,285,287,215,217,219, 221,183,185
8.33	$C_{10}H_7Cl_5$	236,238,240
8.41	Mixture	283,285,287,183,185
8.60	Mixture	236,238,240,318 to 322, 283 to 287

5) The predominant species are the higher chlorinated ones with the Cl_3 species being observed only in the very concentrated species (see Figure C-8). The major component has a minimum of 4 Cl's (see Figure C-9). No parent heptachlor was detected. This confirms earlier on-site GC/EC findings.

6) Endrin feed - The chlorinated (and significant) species observed were endrin and two isomers (see Figure C-10). The other isomers were not dieldrin.

7) Endrin sand column eluents - The only chlorinated species observed were endrin and two isomers (see Figure C-11).

8) Endrin Fe/Cu column eluent - The chlorinated species observed as follows:

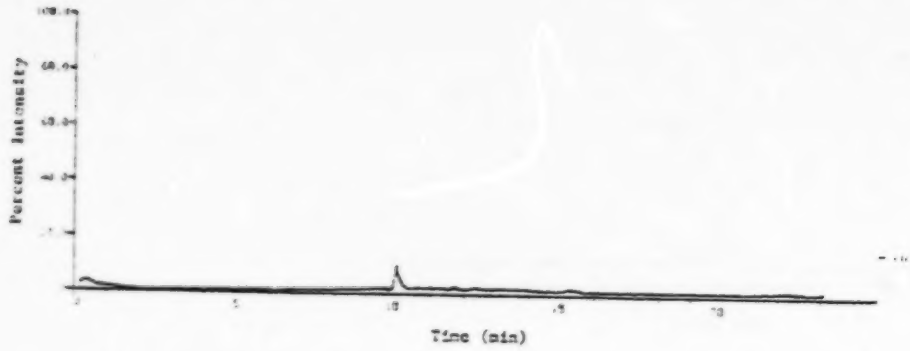

Figure C-6. Total ion current chromatogram of electron impact GC/MS analysis of heptachlor feed solution extract (sample no. 3, 1.0 ml).

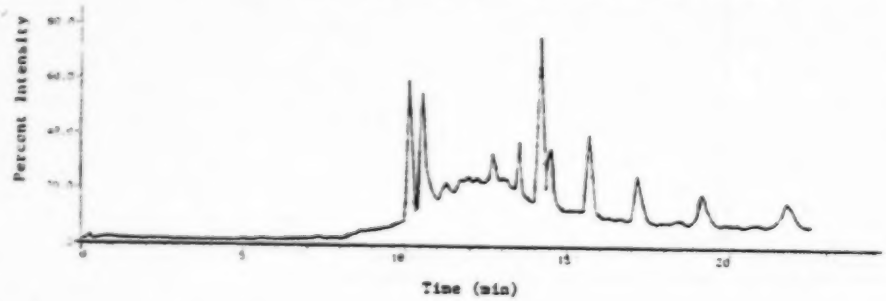

Figure C-7. Total ion current chromatogram of electron impact GC/MS analysis of eluate from sand column with heptachlor feed (sample no. 1, 1.0 ml).

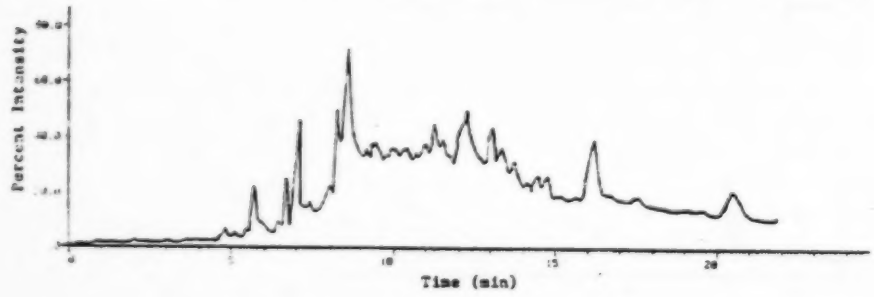

Figure C-8. Total ion current chromatogram of electron impact GC/MS analysis of concentrated eluate from copper/iron column with heptachlor feed (sample no. 2, 0.1 ml).

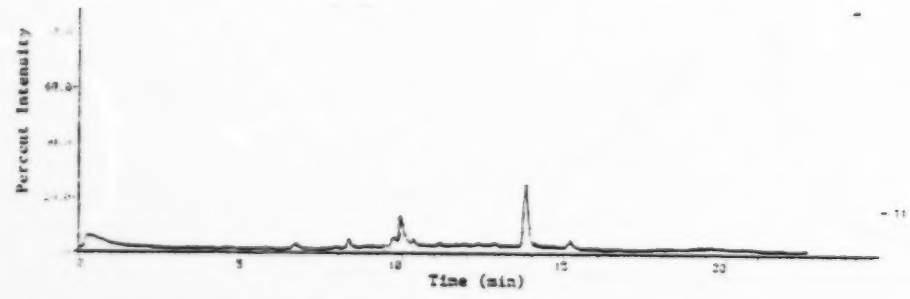

Figure C-9. Total ion current chromatogram of electron impact GC/MS analysis of eluate from copper/iron column with heptachlor feed (sample no. 2, 1.0 ml).

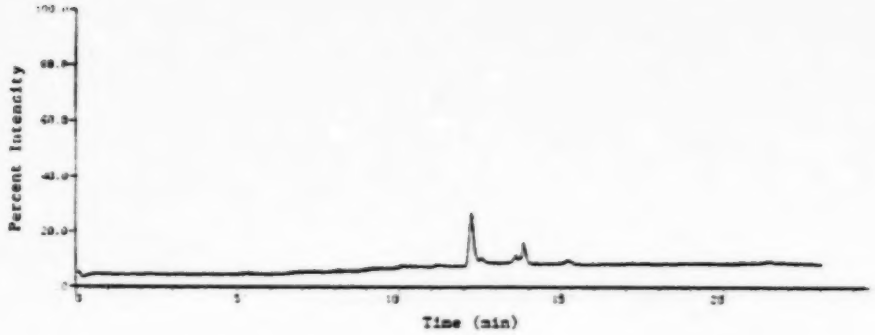

Figure C-10. Total ion current chromatogram of electron impact GC/MS analysis of endrin feed solution extract (sample no. 5, 1.0 ml).

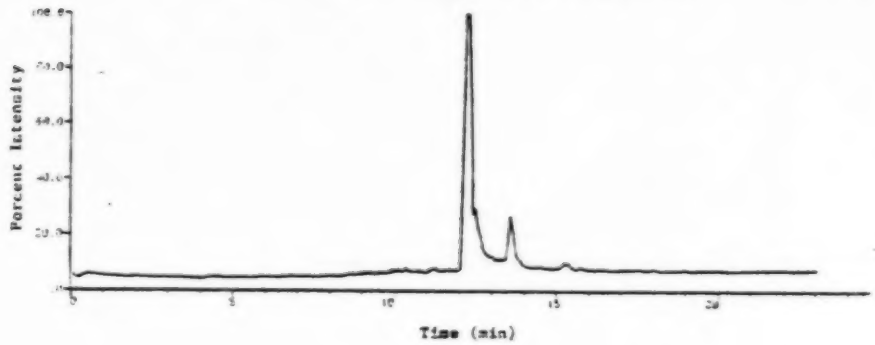

Figure C-11. Total ion current chromatogram of electron impact GC/MS analysis of eluate from sand column with endrin feed (sample no. 4, 1.0 ml).

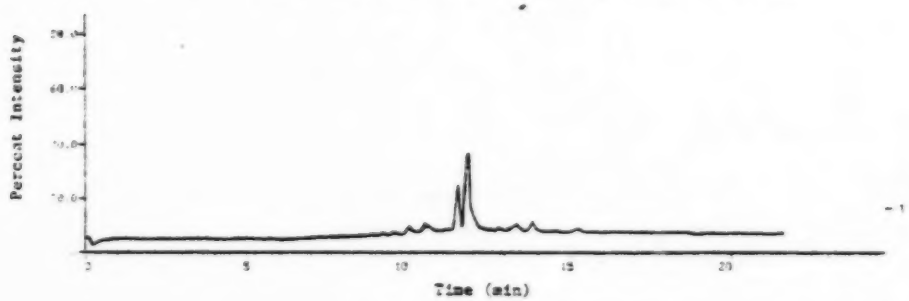

Figure C-12. Total ion current chromatogram of electron impact GC/MS analysis of eluate from copper/iron column with endrin feed (sample no. 6, 1.0 ml).

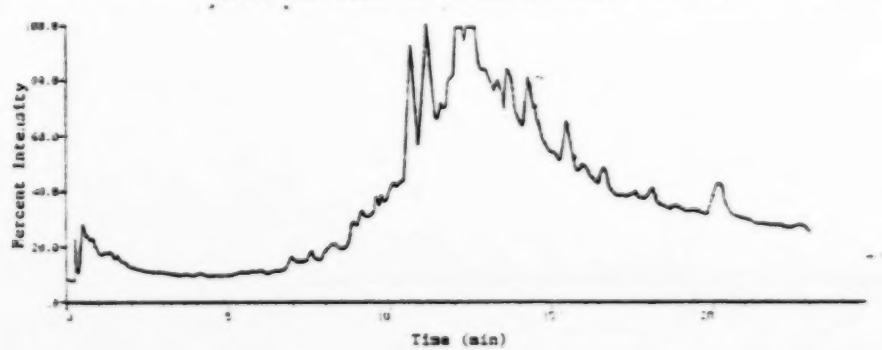

Figure C-13. Total ion current chromatogram of electron impact GC/MS analysis of concentrated eluate from copper/iron column with endrin feed (sample no. 6, 0.1 ml).

Figure C-12. Endrin eluate concentrated to 1.0 ml.

Retention Time (min)	Tentative I.D.	Characteristic Ions
10.49	$C_{12}H_{10}Cl_4O$	310,312,314,275,277,247, 249,211,213
11.49	$C_{12}H_9Cl_5O$	344,346,348,309,311,313, 281,283,285,245,247,209,211
11.83	$C_{12}H_9Cl_5O$	344,346,348,309,311,313, 281,283,285,245,247,209,211
13.33	$C_{12}H_9Cl_5O$	245,247,281,283,285,309, 311,313

Figure C-13. Endrin eluate concentrated to 100 µl.

Retention Time (min)	Tentative I.D.	Characteristic Ions
9.66	$C_{12}H_{12}Cl_2O$	207,209
9.74	$C_{12}H_{11}Cl_3O$	241,243
10.66	$C_{12}H_{11}Cl_3O$	276,278,241,243
11.08	$C_{12}H_{10}Cl_4O$	275,277,279,240,242,310, 312,314
11.74	$C_{12}H_{10}Cl_4O$	275,277,279,310,312,314
12.00	$C_{12}H_9Cl_5O$	309,311,313
13.66	$C_{12}H_9Cl_5O$	245,247,281,283,309,311,313

The major chlorinated species again are the higher chlorinated ones (see Figure C-12). The major peaks in the dilute sample are the ones at 11.49 and 11.83 where only one chlorine has been lost. No endrin was observed again confirming earlier GC/EC analysis. The identifications for the lower chlorinated species in the concentrated samples are extremely tentative due to high background (see Figure C-13).

CONCLUSIONS

- No conversion or reactions were observed on either sand column (no catalyst present) for endrin or heptachlor, i.e., the major component remaining was parent endrin or heptachlor.

- An immediate change in the parent endrin and heptachlor was observed in the Fe/Cu columns.

- Effluent from the Fe/Cu endrin experiment was shown by on-site gas chromatography not to contain parent endrin. This absence of parent endrin was later confirmed by GC/MS analysis at RTI.

- The evaluation of the reduction of heptachlor and endrin showed the test procedure worked, although apparently not well enough to efficiently reduce the pesticides to hydrocarbons and mono-and dichlorinated species.

- The biodegradability and toxicity of chlorinated compounds is a function of the degree of chlorination. The extent of biodegradability is predicated on reduction to mono- or di-chlorinated compounds. Based on the above requirements and the results of various controlled experiments, the effluents generated by this technology would not be environmentally acceptable.